

(19)



(11)

EP 3 719 575 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
07.10.2020 Bulletin 2020/41

(51) Int Cl.:
G03F 1/26 (2012.01) G03F 1/32 (2012.01)

(21) Application number: **20163731.1**

(22) Date of filing: **17.03.2020**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(71) Applicant: **Shin-Etsu Chemical Co., Ltd.**
Tokyo (JP)

(72) Inventor: **KOSAKA, Takuro**
Joetsu-shi,, Niigata (JP)

(74) Representative: **Mewburn Ellis LLP**
Aurora Building
Counterslip
Bristol BS1 6BX (GB)

(30) Priority: **29.03.2019 JP 2019067065**
14.06.2019 JP 2019111026

(54) **PHASE SHIFT MASK BLANK AND PHASE SHIFT MASK**

(57) Provided is a phase shift mask blank including a substrate, and a phase shift film thereon, the phase shift film composed of a material containing silicon and nitrogen and free of a transition metal, the phase shift film including at least one compositionally graded layer having a composition continuously varying in a thickness direction, and a refractive index n and an extinction co-

efficient k , with respect to exposure light, varying in the thickness direction, the exposure light being KrF excimer laser, the compositionally graded layer having a difference between a maximum refractive index $n(H)$ and a minimum refractive index $n(L)$ of up to 0.40, and a difference between a maximum extinction coefficient $k(H)$ and a minimum extinction coefficient $k(L)$ of up to 1.5.

EP 3 719 575 A1

Description

TECHNICAL FIELD

[0001] The invention relates to phase shift mask blanks and phase shift masks, typically used for manufacturing semiconductor integrated circuits.

BACKGROUND

[0002] In a photolithography technique used in a semiconductor technology, a phase shift method is used as one of a resolution enhancement technology. The phase shift method is a contrast enhancing method by forming a phase shift film pattern disposed on a transparent substrate being a photomask substrate which is transparent to exposure light, and utilizing interference of lights. The phase shift film pattern has a phase shift of approximately 180° that is a difference between a phase through the phase shift film and a phase through a portion where the phase shift film is not formed, in other word, a phase through air having a length same as the thickness of the phase shift film. A halftone phase shift mask is one of the photomasks employing such method. The halftone phase shift mask includes a transparent substrate made of quartz or the like which is transparent to exposure light, and a mask pattern of a halftone phase shift film which is formed on the transparent substrate and has a phase shift of approximately 180° relative to a phase through a portion not formed with the phase shift film, and a transmittance substantively insufficient to contribute to exposure in photolithography. As a phase shift film for a halftone phase shift mask, a film containing molybdenum and silicon is mostly used. As such a film, a halftone phase shift film composed of molybdenum silicon oxide or molybdenum silicon oxynitride is known (JP-A H07-140635 (Patent Document 1)).

Citation List

[0003]

Patent Document 1: JP-A H07-140635

Patent Document 2: JP-A 2007-33469

Patent Document 3: JP-A 2007-233179

Patent Document 4: JP-A-2007-241065

DISCLOSURE OF INVENTION

[0004] For phase shift masks and their blanks for use with KrF excimer laser (wavelength of 248 nm) as exposure light in the photolithography, a phase shift film composed of a material containing molybdenum and silicon, and having a phase shift of 180° and a transmittance of approximately 6%, is generally used. In this case, the

phase shift film has a thickness of approximately 100 nm. Recently, for a phase shift film used with ArF excimer laser (wavelength of 193 nm) as exposure light, a phase shift film of silicon nitride has been used for the purposes of minimizing film thickness and for enhancing washing resistance and light resistance. Although not as much as with exposure light of ArF excimer laser, also when KrF excimer laser is used as the exposure light, a phase shift film having high washing resistance and high light resistance and with low tendency to generate haze is needed.

[0005] When a phase shift film to be used with KrF excimer laser as exposure light is made of silicon nitride, if the phase shift film is formed as a single layer having a single composition (uniform composition in the thickness direction) having a refractive index n and an extinction coefficient k corresponding to a phase shift of 170° to 190° and a transmittance of 4 to 8%, the film is formed under film-forming conditions of an unstable regime (the so-called transition mode region) employed in reactive sputtering. As a result, the film has a problem that the in-plane uniformity of the optical characteristics may not be good.

[0006] Meanwhile, to obtain a film having high in-plane uniformity of optical characteristics, it is conceivable that a phase shift film composed of silicon nitride is constructed as a multilayer consisting of layers each having a single composition (uniform composition in the thickness direction) and formed by reactive sputtering under film-forming conditions in a stable region (the so-called metal mode, or the reaction mode). However, the refractive index n of a film formable under this region is lower than a refractive index n of a film formed under the transition mode region, so the film needs to be made thicker. In photolithography, a thin phase shift film is advantageous in forming a finer pattern, and further can reduce undesirable three-dimensional effects. Consequently such a thick film constructed as a multilayer is disadvantageous. Further, in the case of a multilayer consisting of layers formed under film-forming conditions in the stable region, the compositions of the layers are significantly different in every layer. So there is a concern that, in processing the film, the cross-sectional shape of a pattern is deteriorated due to the difference in etching rate.

[0007] The present invention has been made to address the above issues. It is desired to provide a phase shift mask blank and a phase shift mask, including a thin phase shift film having high uniformity in plane, and satisfying a requirement for pattern miniaturization, which is advantageous in terms of patterning and reduction of three-dimensional effects, and satisfying necessary phase shift and transmittance for the phase shift film even when the exposure light is KrF excimer laser having a wavelength of 248 nm.

[0008] The inventor has found that, when a phase shift film is composed of a material containing silicon and nitrogen and free of transition metal and includes a compositionally graded layer having a composition continuously varying in the thickness direction and having optical

constants, with respect to exposure light, varying in the thickness direction, a film having a phase shift amount (phase shift) of 170 to 190° and a transmittance of 4 to 8% can be formed without thickening the film of a phase shift mask blank used with exposure light of KrF excimer laser (wavelength of 248 nm), whereby a phase shift mask blank and a phase shift mask including the phase shift film having high in-plane uniformity of optical characteristics can be obtained.

[0009] In one aspect, the invention provides a phase shift mask blank including a substrate, and a phase shift film thereon, the phase shift film composed of a material containing silicon and nitrogen and free of a transition metal, wherein

the phase shift film includes at least one compositionally graded layer having a composition continuously varying in a thickness direction, and a refractive index n and an extinction coefficient k , with respect to exposure light, varying in the thickness direction, the exposure light being KrF excimer laser,

the compositionally graded layer has a difference between a maximum refractive index $n(H)$ and a minimum refractive index $n(L)$ of up to 0.40, and a difference between a maximum extinction coefficient $k(H)$ and a minimum extinction coefficient $k(L)$ of up to 1.5.

[0010] Preferably, the compositionally graded layer has a minimum refractive index $n(L)$ of at least 2.3 and a maximum extinction coefficient $k(H)$ of up to 2.

[0011] Preferably the phase shift film includes a zone (thickness region) satisfying a refractive index n of at least 2.55 and an extinction coefficient k of up to 1.0, with a thickness of 5 to 30 nm.

[0012] Preferably, the compositionally graded layer has a zone continuously varying a content ratio $N/(Si+N)$ within a range of 0.2 to 0.57 in a thickness direction, the ratio $N/(Si+N)$ representing nitrogen content (at%) to the sum of silicon and nitrogen contents (at%).

[0013] Preferably, the compositionally graded layer has a difference between a maximum silicon content (at%) and a minimum silicon content (at%) of up to 30.

[0014] Preferably, the phase shift film has a phase shift of 170 to 190° and a transmittance of 4 to 8%, in the phase shift film, a ratio of a difference between a maximum phase shift and a minimum phase shift to an average phase shift in plane of up to 3 %, and a ratio of a difference between a maximum transmittance and a minimum transmittance to an average transmittance in plane of up to 5%, and the phase shift film has a thickness of up to 90 nm.

[0015] Preferably, the material containing silicon and nitrogen and free of a transition metal is a material consisting of silicon and nitrogen.

[0016] Typically, the phase shift mask blank may include a second layer consisting of a single layer or multiple layers on the phase shift film, the second layer being composed of a chromium-containing material.

[0017] In other aspects, the invention provides a phase shift mask manufactured by using the phase shift mask

blank, and a method of making a photomask from the blank..

ADVANTAGEOUS EFFECTS

[0018] We find that by means of the proposals herein, there can be provided phase mask blanks and phase shift masks having thin phase shift films which are advantageous in terms of patterning and exposure and have high in-plane uniformity of optical characteristics, while satisfying necessary phase shift and transmittance requirements for use of the phase shift films in exposure light of KrF excimer laser.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

FIGS. 1A and 1B are cross-sectional views illustrating an exemplary phase shift mask blank and a phase shift mask embodying the invention.

FIGS. 2A to 2C are cross-section views illustrating other examples of a phase shift mask blanks.

FURTHER EXPLANATIONS; OPTIONS AND PREFERENCES

[0020] The phase shift mask blank of the invention includes a transparent substrate such as a quartz substrate, and a phase shift film provided on the transparent substrate. The phase shift mask of the invention includes a transparent substrate such as a quartz substrate, and a mask pattern (photomask pattern) of a phase shift film which is provided on the transparent substrate.

[0021] The transparent substrate in the invention is preferably, for example, a 6 inch square, 0.25 inch thick transparent substrate, called 6025 substrate specified by the SEMI standard, which is often denoted by a 152 mm square, 6.35 mm thick transparent substrate, according to the SI unit system.

[0022] FIG. 1A is a cross-sectional view illustrating an exemplary phase shift mask blank of the invention. In this embodiment, a phase shift mask blank 100 includes a transparent substrate 10, and a phase shift film 1 formed on the transparent substrate 10. FIG. 1B is a cross-sectional view illustrating an exemplary phase shift mask of the invention. In this embodiment, the phase shift mask 101 includes the transparent substrate 10, and a phase shift film pattern 11 formed on the transparent substrate 10. A phase shift mask can be obtained by using a phase shift mask blank and forming a pattern of its phase shift film.

[0023] The phase shift film in the invention, with a prescribed thickness, has a predetermined phase shift amount (phase shift) and a predetermined transmittance, with respect to exposure light of KrF excimer laser (wavelength: 248 nm). The phase shift film of the invention is composed of a material containing silicon and nitrogen

and free of a transition metal. To improve washing resistance of the film, it is effective to add oxygen to the phase shift film. Thus, the material containing silicon and nitrogen and free of a transition metal may contain oxygen in addition to silicon and nitrogen. It may consist essentially of (consist of) silicon, nitrogen and oxygen (plus any impurities). However, the refractive index n of the film is reduced when oxygen is added, so that the film thickness tends to be increased. Therefore, as the material containing silicon and nitrogen and free of transition metal, a material consisting essentially of silicon and nitrogen (a material consisting of the two elements and inevitable impurities) is preferable.

[0024] The phase shift film preferably consists of a single layer which is designed so as to satisfy necessary phase shift and transmittance requirements for the phase shift film. The phase shift film may alternatively consist of a plurality of layers which are designed so as to satisfy necessary phase shift and transmittance requirements for the phase shift film as a whole. In either case (single layer, plurality of layers) the phase shift film is constructed so that the film includes at least one compositionally graded layer having a composition continuously varying in the thickness direction, and a refractive index n and extinction coefficient k , with respect to exposure light, also varying in the thickness direction. In case of the plurality of layers, although the film may be constructed of a plurality of the compositionally graded layers or of a combination of one or more compositionally graded layers and one or more single-composition layers (a layer not varying in the thickness direction), the total thickness contributed by the compositionally graded layer(s) is preferably at least 30%, more preferably at least 50% and most preferably 100% of the whole thickness of the phase shift film.

[0025] In the compositionally graded layer, a difference between a maximum refractive index $n(H)$ and a minimum refractive index $n(L)$ is preferably up to 0.40, more preferably up to 0.25, and preferably at least 0.1, more preferably 0.15. In the compositionally graded layer, a difference between a maximum extinction coefficient $k(H)$ and a minimum extinction coefficient $k(L)$ of up to 1.5, more preferably up to 1.2, and preferably at least 0.3, more preferably at least 0.6. The minimum refractive index $n(L)$ in the compositionally graded layer is preferably at least 2.3, more preferably at least 2.4, and the maximum extinction coefficient $k(H)$ is preferably up to 2, more preferably up to 1.5. Particularly, in the compositionally graded layer, the thickness of a zone satisfying a refractive index n of at least 2.55 and an extinction coefficient k of up to 1.0 is preferably at least 5 nm. It is preferably up to 30 nm. This zone thickness contribution may optionally apply to combined plural layers.

[0026] In a compositionally graded layer herein, a compositionally graded range of silicon content is preferably at least 40 at%, particularly at least 45 at%. It is preferably up to 70 at%, particularly up to 60 at%. A compositionally graded range of nitrogen content is preferably at least 30

at%, particularly at least 40 at%. It is preferably up to 60 at%, particularly up to 55 at%. These preferred contents apply for the whole of the compositionally graded layer when the phase shift film is constructed by a single layer, and in each or all or the combination of the layers when the phase shift film is constructed by a plurality of the compositionally graded layers.

[0027] In particular, the compositionally graded layer preferably includes a zone with continuous variation of a content ratio $N/(Si+N)$ which represents nitrogen content (at%) relative to the sum of silicon and nitrogen contents (at%), within a range of preferably at least 0.2, more preferably at least 0.3. It is preferably up to 0.57, more preferably 0.55. The difference between a maximum silicon content (at%) and a minimum silicon content (at%) in the compositionally graded layer is preferably up to 30, more preferably up to 15. In case the compositionally graded layer contains oxygen, the oxygen content is preferably up to 30 at%, more preferably up to 10 at%, most preferably up to 5 at%.

[0028] The phase shift of the exposure light which passes through the phase shift film in the invention may be enough to be able to increase contrast at the boundary between an area having the phase shift film (phase shift area) and an area without the phase shift film, as a result of phase shift due to interference of exposure lights passing through the respective areas. The phase shift may be at least 170° and up to 190° . Meanwhile, a transmittance of the phase shift film in the invention may be at least 4% and up to 8% with respect to exposure light. The phase shift film in the invention may have the phase shift and the transmittance with respect to KrF excimer laser (wavelength: 248 nm), controlled within the aforementioned range.

[0029] The phase shift film is constructed so as to include at least one compositionally graded layer having a composition continuously varying in a thickness direction, and a refractive index n and an extinction coefficient k , with respect to exposure light, varying in the thickness direction. According to the phase shift film of the invention, a variation range of the phase shift, being a ratio of the difference between maximum and minimum phase shifts to the average phase shift, in-plane (over the optically significant region of the blank, for example, within a 135 mm square area at the center of a substrate surface for a 6025 substrate) of the phase shift film, may be up to 3%, particularly up to 1%. A variation range of the transmittance, being a ratio of the difference between the maximum and minimum transmittances to the average transmittance, in-plane of the phase shift film, may be up to 5%, particularly up to 3%.

[0030] When a whole thickness of the phase shift film is thin, fine patterns can be readily formed. Thus, the whole thickness of the phase shift film in the invention is up to 90 nm, preferably up to 85 nm. Meanwhile, the lower limit of the thickness of the phase shift film may be set so long as the desired optical characteristics may be obtained with exposure light, and is typically at least 50

nm, however not limited thereto.

[0031] The phase shift film in the invention may be formed by known methods for forming film. The phase shift film is preferably formed by sputtering by which highly homogenous film is easily obtainable, and the sputtering may be either DC sputtering or RF sputtering. Target and sputtering gas are properly selected depending on kind and composition of the layer to be formed. Examples of the target include silicon target, silicon nitride target, and a target containing both of silicon and silicon nitride. These targets may contain oxygen. The nitrogen content and the oxygen content may be controlled by reactive sputtering using any of reactive gases as a sputtering gas such as a nitrogen-containing gas, an oxygen-containing gas, and a nitrogen and oxygen-containing gas under properly controlling an amount of feeding. In particular, nitrogen gas (N₂ gas), oxygen gas (O₂ gas), and nitrogen oxide gases (N₂O gas, NO gas and NO₂ gas) may be used for the reactive gas. Rare gases such as helium gas, neon gas and argon gas are also employable as the sputtering gas.

[0032] The phase shift film when consisting of multiple layers may include an oxidized surface layer formed as the outermost layer on the top face (on the side remote from the transparent substrate), for the purpose of suppressing change of properties of the phase shift film. The oxidized surface layer may have an oxygen content of at least 20 at%, preferably at least 50 at%. Examples of methods for forming the oxidized surface layer specifically include atmospheric oxidation (natural oxidation); and forced oxidation treatment such as treatment of a sputtered film with ozone gas or ozonated water, or heating at least 300°C in an oxygen-containing atmosphere such as oxygen gas atmosphere, by heating in oven, lamp annealing or laser heating. The oxidized surface layer preferably has a thickness of up to 10 nm, more preferably up to 5nm, most preferably up to 3 nm. An effect of the oxidized surface layer is obtainable typically with a thickness of at least 1 nm. While the oxidized surface layer may be formed by sputtering under an increased oxygen level, the oxidized surface layer is more preferably formed by the aforementioned atmospheric oxidation or oxidation treatment in terms of obtaining the layer with fewer defects. The oxygen of this layer is optionally disregarded for the composition.

[0033] The phase shift mask blank of the invention may include a second layer consisting of a single layer or multiple layers, and formed over the phase shift film. The second layer is usually provided adjacent to the phase shift film. The second layer is specifically exemplified by a light shielding film, a combination of a light shielding film and an antireflection film, and a process-aid film that functions as a hard mask in the process of patterning the phase shift film. In case where a third layer is employed as described below, the second layer may be used as a process-aid film that functions as an etching stopper (etching stopper film) in the process of patterning the third layer. The material of the second layer is preferably

a chromium-containing material.

[0034] This embodiment is specifically exemplified by a phase shift mask blank illustrated in FIG. 2A. FIG. 2A is a cross-sectional view illustrating an exemplary phase shift mask blank of the invention. In this embodiment, a phase shift mask blank 100 includes a transparent substrate 10, a phase shift film 1 formed on the transparent substrate 10, and a second layer 2 formed on the phase shift film 1.

[0035] The phase shift mask blank of the invention may include a light shielding film or an etching mask film which functions as a hard mask when a pattern is formed to a phase shift film, as the second layer, provided over the phase shift film. Alternatively, a light shielding film and an antireflection film may be combined to form the second layer. The second layer including a light shielding film can provide an area that is fully block the exposure light in a phase shift mask. The light shielding film and the antireflection film may also be used as a process-aid film in the etching. There are many reports regarding film structure and materials for the light shielding film and antireflection film (JP-A 2007-33469 (Patent Document 2), JP-A 2007-233179 (Patent Document 3), for example). Preferred film structure having the light shielding film and the antireflection film combined therein is exemplified by a structure in which a light shielding film composed of a chromium-containing material is provided, and an antireflection film composed of a chromium-containing material for reducing reflection from the light shielding film is further provided. The light shielding film and the antireflection film may consist of a single layer or multiple layers. Examples of the chromium-containing material of the light shielding film and the antireflection film include chromium (simple substance), and a chromium compound such as chromium oxide (CrO), chromium nitride (CrN), chromium carbide (CrC), chromium oxynitride (CrON), chromium oxycarbide (CrOC), chromium nitride carbide (CrNC) and chromium oxynitride carbide (CrONC). Notably, the chemical formulae that represent the chromium-containing materials merely denote constituent elements, rather than compositional ratios of the constituent elements (the same shall apply to the chromium-containing materials hereinafter).

[0036] For the second layer as the light shielding film, or the combination of a light shielding film and an antireflection film, the chromium compound in the light shielding film has a chromium content of preferably at least 40 at%, more preferably at least 60 at%, and preferably less than 100 at%, more preferably up to 99 at%, most preferably up to 90 at%. The oxygen content is preferably up to 60 at%, more preferably up to 40 at%, and preferably at least 1 at%. The nitrogen content is preferably up to 50 at%, more preferably up to 40 at%, and preferably at least 1 at%. The carbon content is preferably up to 20 at%, more preferably up to 10 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. In this case, a total content of chromium, oxygen, nitrogen and carbon is preferably at least 95 at%, more preferably at

least 99 at%, and most preferably 100 at%.

[0037] For the second layer as the combination of a light shielding film and an antireflection film, the antireflection film is preferably composed of a chromium compound, and the chromium compound has a chromium content of preferably at least 30 at%, more preferably at least 35 at%, and up to 70 at%, more preferably up to 50 at%. The oxygen content is preferably up to 60 at%, and preferably at least 1 at%, more preferably at least 20 at%. The nitrogen content is preferably up to 50 at%, more preferably up to 30 at%, and preferably at least 1 at%, more preferably at least 3 at%. The carbon content is preferably up to 20 at%, more preferably up to 5 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. In this case, a total content of chromium, oxygen, nitrogen and carbon is preferably at least 95 at%, more preferably at least 99 at%, most preferably 100 at%.

[0038] For a second layer as a light shielding film, or the combination of a light shielding film and an antireflection film, the second layer has a thickness of usually 20 to 100 nm, and preferably 40 to 70 nm.

[0039] A total optical density of the phase shift film and the second layer is preferably at least 2.0, more preferably at least 2.5, most preferably at least 3.0, with respect to exposure light.

[0040] Over the second layer of the phase shift mask blank of the invention, a third layer consisting of a single layer or multiple layers may be provided. The third layer is usually provided adjacent to the second layer. The third layer is specifically exemplified by a process-aid film that functions as a hard mask in the process of patterning the second layer, a light shielding film, and a combination of a light shielding film and an antireflection film. A material composing the third layer is preferably a silicon-containing material, particularly a silicon-containing material free of chromium.

[0041] This embodiment is specifically exemplified by a phase shift mask blank illustrated in FIG. 2B. FIG. 2B is a cross-sectional view illustrating an exemplary phase shift mask blank of the invention. In this embodiment, the phase shift mask blank 100 includes a transparent substrate 10, a phase shift film 1 formed on the transparent substrate 10, a second layer 2 formed on the phase shift film 1, and a third layer 3 formed on the second layer 2.

[0042] For the second layer as the light shielding film, or the combination of a light shielding film and an antireflection film, a process-aid film (etching mask film) which functions as a hard mask in the process of patterning the second layer may be provided as the third layer. In case where a fourth layer is employed as described below, the third layer may be used as a process-aid film that functions as an etching stopper (etching stopper film) in the process of patterning the fourth layer. The process-aid film is preferably composed of a material that differs in etching characteristics from the second layer, such as a material resistant to chlorine-based dry etching for a chromium-containing material, in particular, a silicon-containing material which can be etched by fluorine-con-

taining gases such as SF₆ and CF₄. Examples of the silicon-containing material include silicon (simple substance), and a silicon compound such as a material containing silicon, and either or both of nitrogen and oxygen, a material containing silicon and a transition metal, and a material containing silicon, and either or both of nitrogen and oxygen with a transition metal. Examples of the transition metal include molybdenum, tantalum and zirconium.

[0043] For the third layer as the process-aid film, the process-aid film is preferably composed of a silicon compound. The silicon compound has a silicon content of preferably at least 20 at%, more preferably at least 33 at%, and preferably up to 95 at%, and more preferably up to 80 at%. The nitrogen content is preferably up to 50 at%, more preferably up to 30 at%, and preferably at least 1 at%. The oxygen content is preferably up to 70 at%, more preferably up to 66 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%, more preferably at least 20 at%. A transition metal may be contained or not in the third layer. When the transition metal is contained the transition metal content is preferably up to 35 at%, more preferably up to 20 at%. In this case, a total content of silicon, oxygen, nitrogen and transition metal is preferably at least 95 at%, more preferably at least 99 at%, most preferably 100 at%.

[0044] For the second layer as the light shielding film, or the combination of a light shielding film and an antireflection film, and for the third layer as the process-aid film, the second layer has a thickness of usually 20 to 100 nm, and preferably 40 to 70 nm, and the third layer typically has a thickness of usually 1 to 30 nm, and preferably 2 to 15 nm. A total optical density of the phase shift film and the second layer are preferably at least 2.0, more preferably at least 2.5, most preferably at least 3.0, with respect to exposure light.

[0045] For the second layer as the process-aid film, a light shielding film may be provided as the third layer. The light shielding film in combination with the antireflection film may be provided as the third layer. In this case, the second layer may be used as a process-aid film (etching mask film) that functions as a hard mask in the process of patterning the phase shift film, and as a process-aid film (etching stopper film) in the process of patterning the third layer. The process-aid film is exemplified by a film composed of a chromium-containing material, such as disclosed in JP-A 2007-241065 (Patent Document 4). The process-aid film may consist of a single layer or multiple layers. Examples of the chromium-containing material of the process-aid film include chromium (simple substance), and a chromium compound such as chromium oxide (CrO), chromium nitride (CrN), chromium carbide (CrC), chromium oxynitride (CrON), chromium oxycarbide (CrOC), chromium nitride carbide (CrNC) and chromium oxynitride carbide (CrONC).

[0046] For the second layer as the process-aid film, the chromium compound in the second layer has a chromium content of preferably at least 40 at%, more prefer-

ably at least 50 at%, and preferably up to 100 at%, more preferably up to 99 at%, most preferably up to 90 at%. The oxygen content is preferably up to 60 at%, more preferably up to 55 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. The nitrogen content is preferably up to 50 at%, more preferably up to 40 at%, and preferably at least 1 at%. The carbon content is preferably up to 20 at%, more preferably up to 10 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. In this case, a total content of chromium, oxygen, nitrogen and carbon is preferably at least 95 at%, particularly at least 99 at%, most preferably 100 at%.

[0047] The light shielding film and the antireflection film as the third layer are preferably composed of a material that differs in etching characteristics from the second layer, such as a material resistant to chlorine-based dry etching for a chromium-containing material, in particular, a silicon-containing material which can be etched by fluorine-containing gases such as SF_6 and CF_4 . Examples of the silicon-containing material include silicon (simple substance), and a silicon compound such as a material containing silicon, and either or both of nitrogen and oxygen, a material containing silicon and a transition metal, and a material containing silicon, and either or both of nitrogen and oxygen with a transition metal. Examples of the transition metal include molybdenum, tantalum and zirconium.

[0048] For the third layer as the light shielding film, or the combination of a light shielding film and an antireflection film, the light shielding film and the antireflection film are preferably composed of a silicon compound. The silicon compound has a silicon content of preferably at least 10 at%, more preferably at least 30 at%, and preferably less than 100 at%, more preferably up to 95 at%. The nitrogen content is preferably up to 50 at%, preferably up to 40 at%, and most preferably up to 20 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. The oxygen content is preferably up to 60 at%, more preferably up to 30 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. The transition metal content is preferably up to 35 at%, preferably up to 20 at%, and preferably at least 1 at%. In this case, a total content of silicon, oxygen, nitrogen and transition metal is preferably at least 95 at%, more preferably at least 99 at%, most preferably 100 at%.

[0049] For the second layer as the process-aid film, and for the third layer as the light shielding film, or the combination of a light shielding film and an antireflection film, the second layer has a thickness of usually 1 to 20 nm, and preferably 2 to 10 nm, and the third layer has a thickness of usually 20 to 100 nm, and preferably 30 to 70 nm. A total optical density of the phase shift film, the second layer and the third layer are preferably at least 2.0, more preferably at least 2.5, most preferably at least 3.0, with respect to exposure light.

[0050] Over the third layer of the phase shift mask blank of the invention, a fourth layer consisting of a single layer or multiple layers may be provided. The fourth layer

is usually provided adjacent to the third layer. The fourth layer is specifically exemplified by a process-aid film that functions as a hard mask in the process of patterning the third layer. A material of the fourth layer is preferably a chromium-containing material.

[0051] This embodiment is specifically exemplified by a phase shift mask blank illustrated in FIG. 2C. FIG. 2C is a cross-sectional view illustrating an exemplary phase shift mask blank of the invention. In this embodiment, the phase shift mask blank 100 includes a transparent substrate 10, a phase shift film 1 formed on the transparent substrate 10, a second layer 2 formed on the phase shift film 1, a third layer 3 formed on the second layer 2, and a fourth layer 4 formed on the third layer 3.

[0052] For the third layer as the light shielding film, or the combination of a light shielding film and an antireflection film, a process-aid film (etching mask film) which functions as a hard mask in the process of patterning the third layer may be provided as the fourth layer. The process-aid film is preferably composed of a material that differs in etching characteristics from the third layer, such as a material resistant to fluorine-based dry etching for a silicon-containing material, in particular, a chromium-containing material which can be etched by chlorine-based gases containing oxygen. The chromium-containing material is exemplified by chromium (simple substance), and a chromium compound such as chromium oxide (CrO), chromium nitride (CrN), chromium carbide (CrC), chromium oxynitride (CrON), chromium oxycarbide (CrOC), chromium nitride carbide (CrNC) and chromium oxynitride carbide (CrONC).

[0053] For the fourth layer as the process-aid film, the fourth layer has a chromium content of preferably at least 40 at%, more preferably at least 50 at%, and preferably up to 100 at%, more preferably up to 99 at%, most preferably up to 90 at%. The oxygen content is preferably up to 60 at%, more preferably up to 40 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. The nitrogen content is preferably up to 50 at%, more preferably up to 40 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. The carbon content is preferably up to 20 at%, more preferably up to 10 at%, and if the etching rate is necessarily adjusted, preferably at least 1 at%. In this case, a total content of chromium, oxygen, nitrogen and carbon is preferably at least 95 at%, more preferably at least 99 at%, most preferably 100 at%.

[0054] For the second layer as the process-aid film, for the third layer as the light shielding film, or the combination of a light shielding film and an antireflection film, and for the fourth layer as the process-aid film, the second layer has a thickness of usually 1 to 20 nm, and preferably 2 to 10 nm, the third layer has a thickness of usually 20 to 100 nm, and preferably 30 to 70 nm, and the fourth layer has a thickness of usually 1 to 30 nm, and preferably 2 to 20 nm. A total optical density of the phase shift film, the second layer and the third layer are preferably at least 2.0, more preferably at least 2.5, most preferably at least

3.0, with respect to exposure light.

[0055] The film composed of the chromium-containing material for the second layer and the fourth layer may be formed by reactive sputtering using a target such as chromium target, or a target containing chromium that is added one or more elements selected from the group consisting of oxygen, nitrogen and carbon, and using a sputtering gas containing a rare gas such as Ar, He and Ne that is properly added with a reactive gas selected from the group consisting of an oxygen-containing gas, a nitrogen-containing gas and a carbon-containing gas, according to a composition of the film to be formed.

[0056] Meanwhile, the film composed of the silicon-containing material for the third layer may be formed by reactive sputtering using a target such as a silicon target, a silicon nitride target, a target containing both of silicon and silicon nitride, a transition metal target, and a composite target of silicon and transition metal, and using a sputtering gas containing a rare gas such as Ar, He and Ne that is properly added with a reactive gas selected from the group consisting of an oxygen-containing gas, a nitrogen-containing gas and a carbon-containing gas, according to a composition of the film to be formed.

[0057] The phase shift mask of the invention may be manufactured by any of usual methods from the phase shift mask blank. From an exemplary phase shift mask blank including a film composed of a chromium-containing material formed as a second layer on a phase shift film, the phase shift mask may be manufactured typically by the following processes.

[0058] First, an electron beam resist film is formed on the second layer of the phase shift mask blank, a pattern is drawn by electron beam, followed by a predetermined operation of development, to obtain a resist pattern. Next, the obtained resist pattern is used as an etching mask, and the resist pattern is transferred to the second layer by chlorine-based dry etching containing oxygen, to obtain a second layer pattern. Next, the obtained second layer pattern is used as an etching mask, and the second layer pattern is transferred to the phase shift film by fluorine-based dry etching, to obtain a phase shift film pattern. In case where a part of the second layer is needed to be remained, another resist pattern that protects such part to be remained is formed on the second layer, and a part of the second layer not protected with the resist pattern is removed by chlorine-based dry etching containing oxygen. The resist pattern is then removed by a usual method to obtain the phase shift mask.

[0059] From an exemplary phase shift mask blank including a light shielding film or a combination of a light shielding film and an antireflection film, composed of a chromium-containing material, as a second layer on a phase shift film, and a process-aid film composed of a silicon-containing material as a third layer on the second layer, the phase shift mask may be manufactured typically by the following processes.

[0060] First, an electron beam resist film is formed on the third layer of the phase shift mask blank, a pattern is

drawn by electron beam, followed by a predetermined operation of development, to obtain a resist pattern. Next, the obtained resist pattern is used as an etching mask, and the resist pattern is transferred to the third layer by fluorine-based dry etching, to obtain a third layer pattern. Next, the obtained third layer pattern is used as an etching mask, and the third layer pattern is transferred to the second layer by chlorine-based dry etching containing oxygen, to obtain a second layer pattern. The resist pattern is then removed, and the obtained second layer pattern is used as an etching mask, and the second layer pattern is transferred to the phase shift film by fluorine-based dry etching, to obtain a phase shift film pattern and to concurrently remove the third layer pattern. Next, another resist pattern that protects a part of the second layer to be remained is formed on the second layer, and a part of the second layer not protected with the resist pattern is removed by chlorine-based dry etching containing oxygen. The resist pattern is then removed by a usual method to obtain the phase shift mask.

[0061] Meanwhile, from an exemplary phase shift mask blank including a process-aid film composed of a chromium-containing material as a second layer on a phase shift film, and a light shielding film or a combination of a light shielding film and an antireflection film, composed of a silicon-containing material, as a third layer on the second layer, the phase shift mask may be manufactured typically by the following processes.

[0062] First, an electron beam resist film is formed on the third layer of the phase shift mask blank, a pattern is drawn by electron beam, followed by a predetermined operation of development, to obtain a resist pattern. Next, the obtained resist pattern is used as an etching mask, and the resist pattern is transferred to the third layer by fluorine-based dry etching, to obtain a third layer pattern. Next, the obtained third layer pattern is used as an etching mask, and the third layer pattern is transferred to the second layer by chlorine-based dry etching containing oxygen, to obtain a second layer pattern that a part where the phase shift film will be removed has been removed. The resist pattern is then removed. Next, another resist pattern that protects a part of the third layer to be remained is formed on the third layer, and the obtained second layer pattern is used as an etching mask, and the second layer pattern is transferred to the phase shift film by fluorine-based dry etching, to obtain a phase shift film pattern, and to concurrently remove a part of the third layer which is not protected with the resist pattern. The resist pattern is then removed by a usual method. Further, the part of the second layer, which is exposed in the part where the third layer has been removed, is then removed by chlorine-based dry etching containing oxygen, to obtain the phase shift mask.

[0063] Further, from an exemplary phase shift mask blank including a process-aid film composed of a chromium-containing material as a second layer on a phase shift film, a light shielding film or a combination of a light shielding film and an antireflection film, composed of a

silicon-containing material, as a third layer on the second layer, and a process-aid film composed of a chromium-containing material, as a fourth layer on the third layer, the phase shift mask may be manufactured typically by the following processes.

[0064] First, an electron beam resist film is formed on the fourth layer of the phase shift mask blank, a pattern is drawn by electron beam, followed by a predetermined operation of development, to obtain a resist pattern. Next, the obtained resist pattern is used as an etching mask, and the resist pattern is transferred to the fourth layer by chlorine-based dry etching containing oxygen, to obtain a fourth layer pattern. Next, the obtained fourth layer pattern is used as an etching mask, and the fourth layer pattern is transferred to the third layer by fluorine-based dry etching, to obtain a third layer pattern. The resist pattern is then removed. Next, another resist pattern that protects a part of the third layer to be remained is formed on the fourth layer, and the obtained third layer pattern is used as an etching mask, and the third layer pattern is transferred to the second layer by chlorine-based dry etching containing oxygen, to obtain a second layer pattern, and to concurrently remove a part of the fourth layer which is not protected with the resist pattern. Next, the second layer pattern is used as an etching mask, and the second layer pattern is transferred to the phase shift film by fluorine-based dry etching, to obtain a phase shift film pattern, and to concurrently remove a part of the third layer which is not protected with the resist pattern. The resist pattern is then removed by a usual method. Further, the part of the second layer, which is exposed in the part where the third layer has been removed, and the part of the fourth layer exposed in the part where the resist pattern has been removed, are then removed by chlorine-based dry etching containing oxygen, to obtain the phase shift mask.

EXAMPLES

[0065] Examples of the invention are given below by way of illustration and not by way of limitation.

Example 1

[0066] A 152 mm square, 6.35 mm thick 6025 quartz substrate was placed in a chamber of a sputtering apparatus, and a single-layer phase shift film composed of SiN that is a compositionally graded layer having a composition continuously varying in the thickness direction, and having optical characteristics varying in the thickness direction, was formed thereon using a silicon target as a sputtering target and argon gas and nitrogen gas as a sputtering gas, under the conditions of a discharge power of 1.9 kW, a flow rate of argon gas of 28 seem, and a flow rate of nitrogen gas continuously varied (increased) from 20 to 44 sccm.

[0067] With respect to KrF excimer laser (wavelength of 248 nm), the compositionally graded layer had a maximum refractive index $n(H)$ of 2.61, a minimum refractive index $n(L)$ of 2.33, and the difference between the refractive indexes n was 0.28. A maximum extinction coefficient $k(H)$ was 1.4, a minimum extinction coefficient $k(L)$ was 0.05, and the difference between the extinction coefficients k was 1.35. The thickness of a zone having a refractive index n of at least 2.55 and an extinction coefficient k in the range of up to 1.0 was approximately 15 nm.

[0068] The film had a continuously varied silicon content of 58.5 at% to 46.8 at%, analyzed by XPS (X-ray photoelectron spectroscopy, the same shall apply hereinafter), in the thickness direction from the quartz substrate side, and the difference between the contents was 11.7. The film had a continuously varied content ratio $N/(Si+N)$ from 0.41 to 0.52 in the thickness direction. The phase shift film had a thickness of 87 nm, a phase shift of 177.5° and a transmittance of 5.9% with respect to KrF excimer laser (wavelength of 248 nm). The variation ranges of the phase shift and the transmittance in-plane were, respectively 0.4% and 1.9%, and were favorable.

Example 2

[0069] A 152 mm square, 6.35 mm thick 6025 quartz substrate was placed in a chamber of a sputtering apparatus, and a single-layer phase shift film composed of SiN that is a compositionally graded layer having a composition continuously varying in a thickness direction, and having optical characteristics varying in the thickness direction, was formed thereon using a silicon target as a sputtering target and argon gas and nitrogen gas as a sputtering gas, under the conditions of a discharge power of 1.9 kW, a flow rate of argon gas of 28 sccm, and a flow rate of nitrogen gas continuously varied from 19 to 43 sccm.

[0070] With respect to KrF excimer laser (wavelength of 248 nm), the compositionally graded layer had a maximum refractive index $n(H)$ of 2.61, a minimum refractive index $n(L)$ of 2.33, and the difference between the refractive indexes n was 0.28. A maximum extinction coefficient $k(H)$ was 1.5, a minimum extinction coefficient $k(L)$ was 0.05 and the difference between the extinction coefficients k was 1.45. The thickness of a zone having a refractive index n of at least 2.55 and an extinction coefficient k in the range of up to 1.0 was approximately 15 nm.

[0071] The film had a continuously varied silicon content of 59.1 at% to 46.5 at%, analyzed by XPS, in the thickness direction from the quartz substrate side, and the difference between the contents was 12.6. The film had a continuously varied content ratio $N/(Si+N)$ from 0.40 to 0.53 in the thickness direction. The phase shift film had a thickness of 85 nm, a phase shift of 176.1° and a transmittance of 5.8%, with respect to KrF excimer laser (wavelength of 248 nm). The variation ranges of the phase shift and the transmittance in-plane were respectively 0.9% and 1.7% and were favorable.

Example 3

[0072] A 152 mm square, 6.35 mm thick 6025 quartz substrate was placed in a chamber of a sputtering apparatus, and a single-layer phase shift film composed of SiON that is a compositionally graded layer having a composition continuously varying in a thickness direction, and having optical characteristics varying in the thickness direction was formed thereon by using a silicon target as a sputtering target, and argon gas, oxygen gas and nitrogen gas as a sputtering gas, under the conditions of a discharge power of 1.9 kW, a flow rate of argon gas of 28 sccm, a flow rate of oxygen gas of 1.0 sccm, and a flow rate of nitrogen gas continuously varied from 19 to 43 sccm.

[0073] With respect to KrF excimer laser (wavelength of 248 nm), the compositionally graded layer had a maximum refractive index $n(H)$ of 2.59, a minimum refractive index $n(L)$ of 2.30, and the difference between the refractive indexes n was 0.29; a maximum extinction coefficient $k(H)$ of 1.4, a minimum extinction coefficient $k(L)$ of 0.05, and the difference between the extinction coefficients k was 1.35, and had a zone having a refractive index n in the range of at least 2.55, an extinction coefficient k in the range of up to 1.0, and a thickness of approximately 14 nm.

[0074] The film had a continuously varied silicon content of 56.7 at% to 45.4 at%, analyzed by XPS, in the thickness direction from the quartz substrate side, and the difference between the contents was 11.3. The film had a continuously varied content ratio $N/(Si+N)$ from 0.42 to 0.52 in the thickness direction. The film had a substantively constant oxygen content of 2 at% in the thickness direction. The phase shift film had a thickness of 88 nm, a phase shift of 177.5° and a transmittance of 6.0%, with respect to KrF excimer laser (wavelength of 248 nm). A variation ranges of the phase shift and the transmittance in-plane were, respectively, 0.4% and 0.8% that were favorable.

Comparative Example 1

[0075] A 152 mm square, 6.35 mm thick 6025 quartz substrate was placed in a chamber of a sputtering apparatus, and a two-layer phase shift film consisting of a lower layer and an upper layer was formed by using a silicon target as a sputtering target, and argon gas and nitrogen gas as a sputtering gas, under the conditions of a discharge power of 1.9 kW, a flow rate of argon gas of 28 seem, and a flow rate of nitrogen of 19 sccm, for the lower layer (thickness: 27 nm) composed of SiN that has a constant composition in the thickness direction and optical characteristics not varying in the thickness direction; and by using the same target and gases under the same conditions other than a changed flow rate of argon gas of 35 sccm, for the upper layer (thickness: 64 nm) composed of SiN that has a constant composition in the thickness direction and optical characteristics not varying in

the thickness direction.

[0076] With respect to KrF excimer laser (wavelength of 248 nm), the lower layer had a refractive index n of 2.45, the upper layer had a refractive index n of 2.38, and the difference between the refractive indexes n was 0.07; the lower layer had an extinction coefficient k of 1.5, the upper layer had an extinction coefficient k of 0.07 and the difference between the extinction coefficients k was 1.43, and there was no zone having a refractive index n in the range of at least 2.55 and an extinction coefficient k in the range of up to 1.0.

[0077] The film had a silicon content of 59.2 at% in the lower layer, and a silicon content of 46.5 at% in the upper layer, analyzed by XPS, and the difference between the contents was 12.7. The film had a content ratio $N/(Si+N)$ of 0.40 in the lower layer, and a content ratio $N/(Si+N)$ of 0.53 in the upper layer. The phase shift film had a phase shift of 177.0° and a transmittance of 6.2%, with respect to KrF excimer laser (wavelength of 248 nm). The variation ranges of the phase shift and the transmittance in-plane were respectively 0.9% and 3.6%, however, the thickness of the film was 91 nm so that the film was formed thick.

Comparative Example 2

[0078] A 152 mm square, 6.35 mm thick 6025 quartz substrate was placed in a chamber of a sputtering apparatus, and a single-layer phase shift film composed of SiN of a constant composition in the thickness direction and optical characteristics not varying in the thickness direction was formed using a silicon target as a sputtering target, and argon gas and nitrogen gas as a sputtering gas, under the conditions of a discharge power of 1.9 kW, a flow rate of argon gas of 28 sccm, and a flow rate of nitrogen of 27 sccm.

[0079] With respect to KrF excimer laser (wavelength of 248 nm), the layer had a refractive index n of 2.60 and an extinction coefficient k of 0.7, and the whole of the layer satisfied a refractive index n in the range of at least 2.55 and an extinction coefficient k in the range of up to 1.0.

[0080] The film had a silicon content of 50.4 at%, analyzed by XPS. The film had a content ratio $N/(Si+N)$ of 0.49. The phase shift film had a thickness of 79 nm, a phase shift of 177.2° and a transmittance of 4.5%, with respect to KrF excimer laser (wavelength of 248 nm). However, the variation ranges of the phase shift and the transmittance in-plane were respectively 0.5% and 11.1%, and this variation range of transmittance was disadvantageous.

Comparative Example 3

[0081] A 152 mm square, 6.35 mm thick 6025 quartz substrate was placed in a chamber of a sputtering apparatus, and a single-layer phase shift film composed of MoSiON of a constant composition in the thickness di-

rection and optical characteristics not varying in the thickness direction was formed using a molybdenum silicon (MoSi) target and a silicon target as a sputtering target, and argon gas, nitrogen gas and oxygen gas as sputtering gas, under the conditions of a discharge power of MoSi target of 1.2 kW, a discharge power silicon target of 8 kW, a flow rate of argon gas of 5 sccm, a flow rate of nitrogen of 65 sccm, and a flow rate of oxygen of 2.5 sccm.

[0082] With respect to KrF excimer laser (wavelength of 248 nm), the layer had a refractive index n of 2.25 and an extinction coefficient k of 0.52. There was no zone having a refractive index n in the range of at least 2.55 and an extinction coefficient k in the range of up to 1.0.

[0083] The film had a molybdenum content of 14 at%, a silicon content of 35 at%, a nitrogen content of 45 at%, and an oxygen content of 6 at%, analyzed by XPS. The phase shift film had a phase shift of 175.1° and a transmittance of 6.2%, with respect to KrF excimer laser (wavelength of 248 nm). The variation ranges of the phase shift and the transmittance in-plane were respectively 0.3% and 1.7%, however, the thickness of the film was 99 nm so that the film was formed thick.

Notes

[0084] In respect of numerical ranges disclosed in the present description it will of course be understood that in the normal way the technical criterion for the upper limit is different from the technical criterion for the lower limit, i.e. the upper and lower limits are intrinsically distinct proposals.

[0085] For the avoidance of doubt it is confirmed that in the general description above, in the usual way the proposal of general preferences and options in respect of different features of the blank, method and mask constitutes the proposal of general combinations of those general preferences and options for the different features, insofar as they are combinable and compatible and are put forward in the same context.

[0086] The entire contents of Japanese Patent Applications 2019-067065 filed on 29 March 2019 and 2019-111026 filed on 14 June 2019, the priorities of which is claimed herein, are hereby incorporated by reference as a precaution in case of error in translation or transcription.

Claims

1. A phase shift mask blank comprising a substrate (10) and a phase shift film (1) thereon, the phase shift film (1) being composed of a material containing silicon and nitrogen and free of transition metal, wherein the phase shift film (1) comprises at least one compositionally graded layer having a composition continuously varying in the thickness direction, and a

refractive index n and an extinction coefficient k , with respect to KrF excimer laser exposure light, which vary in the thickness direction, and wherein the compositionally graded layer has a difference between a maximum refractive index $n(H)$ and a minimum refractive index $n(L)$ which is not more than 0.40, and a difference between a maximum extinction coefficient $k(H)$ and a minimum extinction coefficient $k(L)$ of not more than 1.5.

2. Phase shift mask blank of claim 1, wherein the compositionally graded layer has a minimum refractive index $n(L)$ of at least 2.3 and a maximum extinction coefficient $k(H)$ of up to 2, the compositionally graded layer comprises a zone in which the refractive index n is 2.55 or more and the extinction coefficient k is at least 1.0, and said zone has a thickness of 5 to 30 nm.
3. Phase shift mask blank of claim 1 or 2, wherein the compositionally graded layer has a zone in which a content ratio $N/(Si+N)$ varies continuously in the thickness direction, provided that the variation is within the range 0.2 to 0.57, the ratio $N/(Si+N)$ representing nitrogen content in at% relative to the sum of silicon and nitrogen contents in at%.
4. Phase shift mask blank of any one of claims 1 to 3, wherein in the compositionally graded layer the difference between a maximum silicon content (at%) and a minimum silicon content (at%) is not more than 30.
5. Phase shift mask blank of any one of claims 1 to 4, wherein the phase shift film has a phase shift of 170° to 190° and a transmittance of 4 to 8%, in the phase shift film, a ratio of a difference between a maximum phase shift and a minimum phase shift to an average phase shift in plane of up to 3 %, and a ratio of a difference between a maximum transmittance and a minimum transmittance to an average transmittance in plane of up to 5%, and the phase shift film has a thickness of up to 90 nm.
6. Phase shift mask blank of any one of claims 1 to 5, wherein the material containing silicon and nitrogen and free of transition metal is a material consisting of silicon and nitrogen.

7. Phase shift mask blank of any one of claims 1 to 6 comprising a second layer (2) consisting of a single layer or multiple layers on the phase shift film, the second layer being composed of chromium-containing material.
8. Phase shift mask blank of any one of the preceding claims in which the thickness of the phase shift film is from 50 nm to 90 nm.

9. Phase shift mask blank of any one of the preceding claims in which the total thickness contributed by the compositionally graded layer(s) is at least 50% of the thickness of the phase shift film. 5
10. Phase shift mask blank of any one of the preceding claims in which
- said difference between the maximum refractive index $n(H)$ and minimum refractive index $n(L)$ is at least 0.1, preferably 0.15, and/or 10
 - said difference between the maximum extinction coefficient $k(H)$ and the minimum extinction coefficient $k(L)$ is at least 0.3, preferably at least 0.6. 15
11. A phase shift mask manufactured from a phase shift mask blank of any one of claims 1 to 10.
12. A method of manufacturing a photomask for use with KrF excimer laser as exposure light, the method comprising patterning the phase shift film of a mask blank of any one of claims 1 to 10. 20

25

30

35

40

45

50

55

FIG.1A

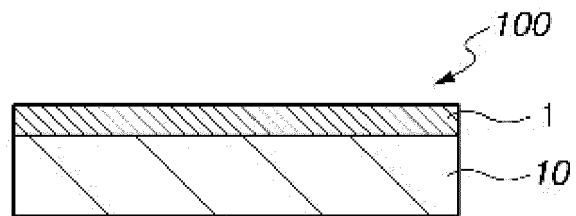


FIG.1B

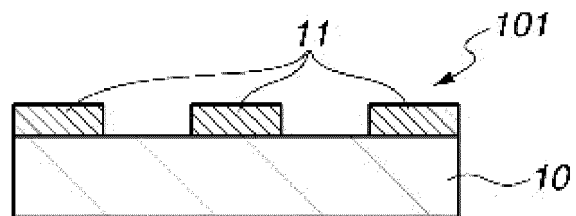


FIG.2A

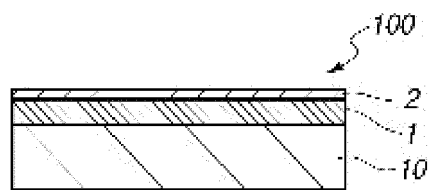


FIG.2B

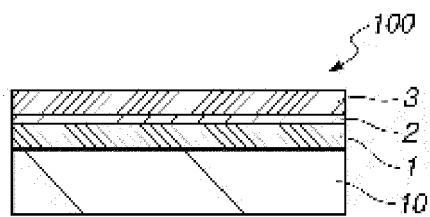
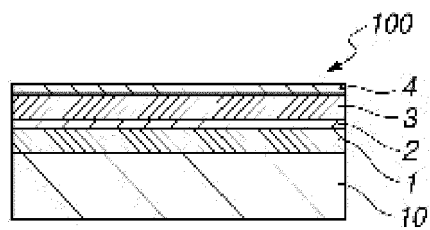


FIG.2C





EUROPEAN SEARCH REPORT

Application Number
EP 20 16 3731

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	JP 2002 040625 A (TOSHIBA CORP) 6 February 2002 (2002-02-06) * paragraphs [0034], [0035], [0040], [0041], [0109], [0141] - [0145]; figure 14 *	1-12	INV. G03F1/26 G03F1/32
X	US 2019/064650 A1 (KOSAKA TAKURO [JP] ET AL) 28 February 2019 (2019-02-28) * paragraphs [0024] - [0029], [0061], [0077] - [0091]; examples 1-5 *	1-12	
Y		1-12	
A	SMITH B W ET AL: "Development and characterization of nitride and oxide based composite materials for sub 0.18 @mm attenuated phase shift masking", MICROELECTRONIC ENGINEERING, ELSEVIER PUBLISHERS BV., AMSTERDAM, NL, vol. 35, no. 1, 1 February 1997 (1997-02-01), pages 201-204, XP004054040, ISSN: 0167-9317, DOI: 10.1016/S0167-9317(96)00121-9 * Sections 1, 3.4, 4 *	1-12	
A	ITO S ET AL: "OPTIMIZATION OF OPTICAL PROPERTIES FOR SINGLE-LAYER HALFTONE MASKS", OPTICAL / LASER MICROLITHOGRAPHY 7. SAN JOSE, MAR. 2 - 4, 1994; [PROCEEDINGS OF SPIE. OPTICAL / LASER MICROLITHOGRAPHY], BELLINGHAM, SPIE, US, vol. VOL. 2197, 2 March 1994 (1994-03-02), pages 99-110, XP000989174, ISBN: 978-0-8194-1492-2 * pages 102,102; figure 8 *	1-12	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 27 August 2020	Examiner Roesch, Guillaume
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 20 16 3731

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

27-08-2020

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2002040625 A	06-02-2002	NONE	
US 2019064650 A1	28-02-2019	CN 106997145 A	01-08-2017
		EP 3196698 A1	26-07-2017
		JP 6500791 B2	17-04-2019
		JP 2017129808 A	27-07-2017
		KR 20170088299 A	01-08-2017
		SG 10201700495Q A	30-08-2017
		TW 201736943 A	16-10-2017
		US 2017212417 A1	27-07-2017
		US 2019064650 A1	28-02-2019

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP H07140635 A [0002] [0003]
- JP 2007033469 A [0003]
- JP 2007233179 A [0003] [0035]
- JP 2007241065 A [0003] [0045]
- JP 2007 A [0035]
- JP 33469 A [0035]
- JP 2019067065 A [0086]
- JP 2019111026 A [0086]